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Pulsed laser deposition as a materials research tool

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Abstract

Pulsed laser deposition (PLD) is currently being used to deposit a variety of multicomponent electronic ceramic thin films as a materials research tool for the development of next generation electronic devices. Examples include $YBa_2Cu_3O_{7-\delta}$/ferromagnetic multilayers, ferroelectrics and rare earth doped manganite thin films. In $YBa_2Cu_3O_{7-\delta}$/ferromagnetic multilayers, the injection of spin-polarized electrons from the ferromagnetic material into the superconductor produces a local reduction in the superconducting order parameter. This effect is being used to develop HTS-based digital logic. The electric field effect in $Sr_xBa_{(1-x)}TiO_3$ thin films is being used to develop tunable microwave circuits. A 4:1 change in the dielectric constant has been observed for fields ≤ 80 kV/cm. Microstructural defects associated with cation and anion vacancies have been observed in $Sr_xBa_{(1-x)}TiO_3$ films. These defects have been correlated with dielectric loss and can be reduced by the use of a compensated targets and a post-deposition anneal of the deposited films. A large temperature coefficient of resistance (TCR) has been observed in rare earth doped manganite thin films. A TCR as large as $\sim 30\%$ has been observed for well annealed $La_{0.67}Ca_{0.33}MnO_\delta$ thin films. These materials can be used to increase the sensitivity of uncooled IR focal plane arrays by more than an order of magnitude making them comparable to HgCdTe detectors. This paper presents the advances in thin film processing and the importance of PLD as a tool for research in the physics of thin films, materials science and the fabrication of devices based on electronic ceramics. © 1998 Elsevier Science B.V.

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1. Introduction

Initial interest in pulsed laser deposition (PLD) focused on the novelty of a simple and versatile physical vapor deposition technique for ceramic, high T_c superconductors (HTS) and later expanded to include other multicomponent oxides such as ferroelectrics and ferrites [1]. The ease with which oxide ceramic materials can now be grown as high-quality thin films now makes PLD an important research tool in physics, materials science and the development of next generation electronics. We report here the use of PLD to investigate the properties of electronic ceramic thin films and multilayers for the development of new devices. These include digital logic based on high-temperature superconducting thin films, frequency agile microwave devices based on ferroelectric thin films, and uncooled infrared imag-

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ing systems based on rare earth doped manganite thin films.

The physics of electronic transport in HTS/ferromagnetic multilayers is currently being investigated for the first time in PLD multilayers. This investigation has led to the discovery that the injection of spin-polarized electrons into an HTS film can produce a local reduction in the superconductivity order parameter [2]. This phenomenon can be used to form unique high-voltage and high-current gain superconducting transistors and serve as the basis for the development of a broad range devices including digital electronics and fast, high-gain HTS-based switches.

The electric field dependence of the dielectric constant in ferroelectric thin films is being used to develop frequency agile microwave electronics. Key to the implementation of these materials will be a detailed understanding of the origin of dielectric loss in these materials at microwave frequencies. It is extremely important to identify the type and distribution of microstructural defects, and to correlate their effect on microwave absorption.

Finally, the recently discovered rare earth doped manganite thin films are being used to develop high-sensitivity, uncooled IR imaging systems. Although the principal interest in these materials is for their large magnetoresistance [3–5], these materials also possess a large temperature-dependent resistivity. IR detectors based on the manganite films could offer sensitivities comparable to cooled semiconducting devices with a significant savings in size, weight, power consumption and cost. In all these systems, PLD has played a significant role in advancing our understanding of the physics of the thin-film structures, the material science of a new system, and the development of new devices.

2. Spin injection

Since the discovery of ceramic superconductors, there have been considerable interest in the fabrication of conventional superconducting electronics from HTS thin films. While HTS thin films of extremely high quality can be deposited by PLD, with the exception of some passive microwave devices, efforts to produce HTS electronics have been without much success. This is due, in large part, to the difficulty encountered in fabricating and processing of HTS thin films and multilayers, and to the tight physical tolerances required for these devices. Some of the approaches to superconducting transistors include: superconducting base transistors, dielectric base transistors, vortex flow transistors, electric field effect devices, and quasiparticle injection devices [6]. These approaches suffer from several difficulties that include: difficulty in fabrication, low gain, slow speed, high noise, and low power handling capabilities. A novel approach to HTS three-terminal devices is to take advantage of the phenomenon known as spin injection. In spin injection devices, spin-polarized conduction electrons are injected from a ferromagnetic material into a normal metal creating a non-equilibrium population of spins in the material. The polarized conduction electron's spin orientation is eventually randomized by spin scattering events. If the polarized injection current is greater than the scattering rate, a non-equilibrium magnetization is obtained in the vicinity of the interface extending a distance known as the spin diffusion length.

Spin-polarized injection has been observed in superconductors: first in low temperature superconductors (LTS) like Nb [7], and more recently in HTS materials ($YBa_2Cu_3O_{7-\delta}$) [2,8]. The injection of a spin-polarized current into a superconductor affects the transport properties by disrupting the equilibrium population of Cooper pairs to a much greater extent than the injection of a similar number of unpolarized electrons [9]. The effect is expected to be larger in a high-temperature superconductor due to one to two order-of-magnitude lower carrier density in HTS than in LTS; however, the higher density of spin scatterers at the HTS/ferromagnetic interface can make it much more difficult to observe the effect.

In our initial attempts to observe spin injection in $YBa_2Cu_3O_{7-\delta}$, the ferromagnetic layer (permalloy) was separated from the $YBa_2Cu_3O_{7-\delta}$ layer by a thin layer of Au [2]. These structures, although clearly demonstrated proof-of-concept, were difficult to fabricate. We report here an improved device. An all oxide structure has been fabricated, as shown in Fig. 1. Replacement of permalloy with $La_xSr_{1-x}MnO_\delta$ offers a source of 100% spin-polarized carriers (compared to $\sim$45% for permalloy) for injection into the superconductor with a thin $SrTiO_3$ layer

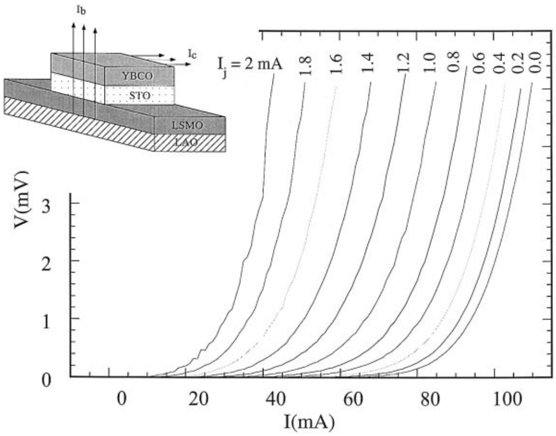

Fig. 1. The current–voltage curves for a $La_xSr_{1-x}MnO_{\delta}/SrTiO_3/YBa_2Cu_3O_{7-\delta}$ deposited trilayer deposited onto a $LaAlO_3$ substrate measured at 77 K with bias currents from 0 to 2 mA in 0.2 mA steps. Film structure is shown in inset.

separating the two materials. Replacement of the conducting Au layer with an insulating, $SrTiO_3$ layer ensures uniform injection of polarized electrons in the junction.

An example of the effect of spin-polarized injection is shown in Fig. 1. The effect is quite large. A bias current (I_b) is proportional to the number density of polarized electrons in the superconductor that suppresses the superconducting energy gap and reduces the critical current in the superconducting film. The current–voltage curves are shown for the sample measured at 77 K with bias currents from 0 to 2 mA in 0.2 mA increments. Unbiased, the superconducting film exhibits a critical current (I_c) of about 80 mA. With a 2-mA bias, the critical current is reduced to about 20 mA. The magnitude of the effect is defined as the current gain (G), which is the change in the critical current, divided by the change in the bias current, $G = \Delta I_c / \Delta I_b$. For the data shown in Fig. 1, the calculated gain for the device is ~ 30. The concept developed here represents a new and unique area of condensed matter physics combining non-equilibrium superconductivity and magneto-transport. The data shows that PLD of HTS/ferromagnetic multilayer thin films can be used to develop a new class of superconducting electronic devices.

3. Ferroelectrics

High-quality ferroelectric thin films offer unique opportunities for the development of advanced microwave signal processing devices [10]. In a ferroelectric, the dielectric constant can be reduced by more than 50% in the presence of a DC electric field. The field-dependent change in the electrical length of a device can be used to produce a shift in the resonant frequency, time delay or a phase shift [10]. Thin films offer an advantage over bulk materials for these applications since large electric fields (0–200 kV/cm) can be achieved using low bias voltages (0–10 V). Several critical issues need to be addressed for the development of thin-film-based microwave devices. These include characterization of dielectric properties at microwave frequencies to determine the dielectric constant, tunability, Curie temperature and dielectric losses. The most critical issue in the development of microwave devices is the reduction of the dielectric loss in the thin film to be at or near to the intrinsic loss of a single crystal.

$Sr_xBa_{(1-x)}TiO_3$ (SBT) is a ferroelectric material that is currently being used for the development of ferroelectric-based microwave electronics because of its low dielectric loss and high tunability. The Curie temperature of bulk SBT ranges from 30 to 400 K for x between 1 and 0 [11]. The ability to control the ferroelectric properties in a simple way will allow device structures to be optimized for maximum tunability and minimum loss at a desired device operating temperature. PLD has been used to produce single-phase, exclusively (001) oriented thin films on $SrTiO_3$ MgO and $LaAlO_3$ substrates [12–15].

The dielectric properties of the $Sr_xBa_{(1-x)}TiO_3$ ferroelectric films deposited by PLD have been measured at 1 MHz as a function of temperature and field using interdigitated capacitors. The interdigital structures are fabricated from e-beam evaporated Ag films, which are deposited through a lift-off mask on top of an SBT. To minimize metal losses at microwave frequencies, the metal is several skin depths thick (~ 3 μm).

Typical data for the behavior of $Sr_xBa_{(1-x)}TiO_3$ ($x = 0.65$) at 1 MHz are shown in Fig. 2. The results for a broad range of x are qualitatively similar. The temperature dependence of the film capacitance (directly proportional to the dielectric constant), is much

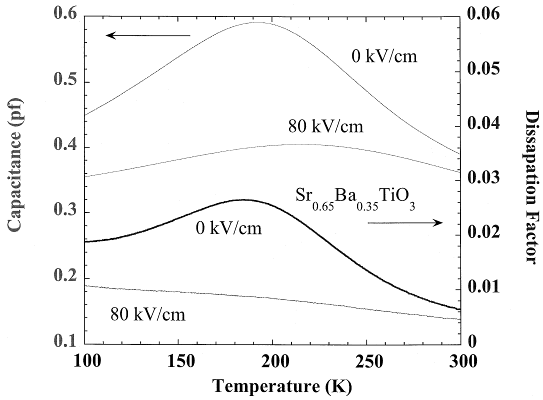

Fig. 2. Capacitance and dissipation factor measured at 1 Mhz for an interdigitated capacitor fabricated from an as-deposited $Sr_{0.65}Ba_{0.35}TiO_3$ thin film.

broader than the corresponding bulk material, and the Curie temperature is reduced for the film relative to the bulk. Unlike the bulk material, the temperature dependence of the dissipation factor has a maximum above the thin film Curie temperature. A second peak is observed in the temperature dependence of the loss (at ~ 50 K), which probably corresponds to the tetragonal to orthorhombic transition seen in the bulk $SrTiO_3$. Measurements on $Sr_xBa_{(1-x)}TiO_3$ tri-layer capacitors indicated that the dielectric constant for the thin film is greatly reduced from the bulk material [16].

The loss tangent for the deposited film has been measured at 1–20 GHz. As-deposited films are characterized with values for tan δ that are ~ 0.01–0.05 compared to $\leq 1 \times 10^{-4}$ for $SrTiO_3$ single crystals. A large field dependence is observed in the thin film with the capacitance being reduced by more than a factor of 2 for fields of ~ 80 kV/cm.

The differences between the thin film and bulk behavior are likely due to several factors but principally due to strain. As-deposited films exhibit significant non-uniform strain [13]. The calculated strain as determined from the broadening of X-ray diffraction peaks is $\sim 0.1\%$ [13]. This is very large for a ceramic material, and it is most likely due to the lattice mismatch between the film and the substrate, and the vacancies of the cation and anion.

Oxygen (anion) vacancies are present, as films are deposited in a relatively low partial pressure of oxygen (~ 300 mTorr). To remove oxygen vacancies, PLD thin films have been post-annealed in flowing oxygen at temperatures from 900°C [13] to 1350°C. After annealing the as-deposited films, significant changes were observed in the structure and dielectric properties. X-ray diffraction of the post-annealed films indicates an decrease in the lattice parameter (presumably due to filling of oxygen vacancies), and a decrease in non-uniform strain. Fig. 3a shows the comparison of the capacitance and dissipation factor as a function of temperature for the as-deposited and 900°C-annealed films of $Sr_{0.65}Ba_{0.35}TiO_3$. The influence of the post-deposition anneal can be seen clearly in several aspects of the data. First, in the capacitance data, we see a narrowing of the temperature dependence of the dielectric constant, indicating more bulk-like behavior in the annealed film. Second, we see a shift in the Curie temperature of the film. The T_c is increased

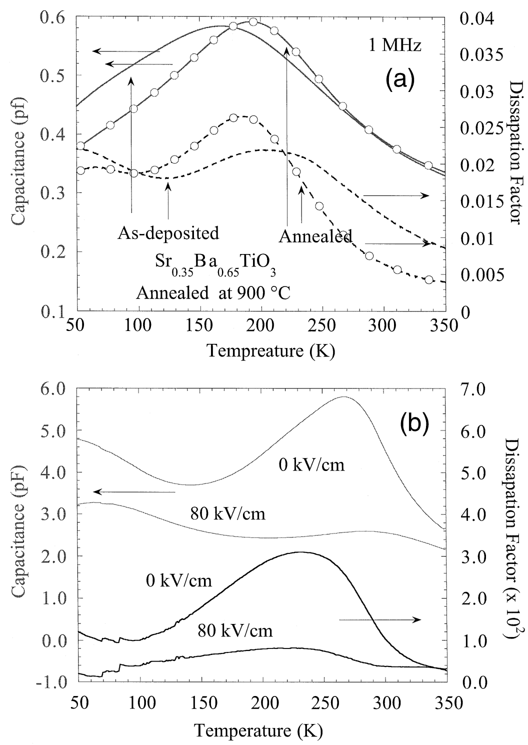

Fig. 3. Capacitance and dissipation factor for measured at 1 Mhz for an interdigitated capacitor fabricated from annealed $Sr_xBa_{(1-x)}TiO_3$ thin films. (a) $x = 0.65$, annealed at 900°C. (b) $x = 0.5$ annealed at 1250°C.

due to annealing from about 170 to 195 K, but is still below the bulk value of ~ 200 K [13].

In addition to the dielectric constant, we see a significant shift in the temperature dependence of the dielectric loss as a function of annealing. Annealing in oxygen shifts the loss maximum to lower temperatures. If the annealing temperature is increased to 1250°C, further improvements of the dielectric behavior at 1 MHz are seen. Shown in Fig. 3b are the temperature dependence of the capacitance and dissipation factor for an $Sr_{0.5}Ba_{0.5}TiO_3$ annealed at 1250°C for 2 h in flowing oxygen. To prevent the loss of volatile components, the film is encased in a ceramic bomb that has the same chemical composition as the deposited film. The dielectric loss peak is shifted to be below the phase transition temperature, as is normally observed in bulk crystals. It is interesting to note that the Curie temperature for the film is now shifted to be above that observed in the bulk. This behavior is likely to be a consequence of strain still present in the post-annealed film.

The dielectric loss at high frequency serves as an extremely sensitive measure of microstructural defects in the ferroelectric thin films. Small changes in the lattice parameter associated with filling of oxygen vacancies yield extremely large changes in the dielectric loss. Preliminary measurements indicate that cation vacancies are also present in the PLD films. Sr and Ba vacancies of 3–11% have been observed in $Sr_xBa_{(1-x)}TiO_3$ films. These vacancies are presumably caused by variations in the metal sticking coefficients since the substrate is exposed to a stoichiometric vapor from the ablated target. For this system, compensation of the target for deficiencies observed in the film composition further reduces the dielectric loss and shifts the peak in the temperature dependence of the loss to lower temperatures. The data indicates that the defect concentration PLD films are approaching the level where they can be used to develop tunable microwave circuits.

4. Rare-earth doped manganites for IRFPAs

Uncooled infrared imaging systems based on microbolometers offer the possibility for the development of a light weight, inexpensive alternative for complex, cooled IR imaging systems based on HgCdTe (MCT) or InSb [17]. The sensitivity of current microbolometer-based systems are an order of magnitude lower than that of semiconducting systems. The active element in the microbolometer-based detector is an oxide-coated silicon microbridge. The oxide film has a temperature-dependent resistance. Heating of the microbridge by the incident IR radiation is detected by a change in the microbridge resistivity. Current microbolometer-based systems use V_xO_y which has a reported temperature coefficient of resistance (TCR) of -2% at room temperature. The discovery of new materials with higher TCRs could increase the sensitivity of the microbolometers to be comparable to MCT detectors. Recently, a new class of oxide materials has been discovered that could be used to replace V_xO_y in microbolometer-based detectors. Large temperature-dependent resistivities have been observed in the rare earth doped manganites, $RE_xM_{1-x}MnO_\delta$, where M = Sr, Ba, Ca, Pb; and RE = Pr, Nd, La [18].

The recent interest in the rare earth manganites is not due to its TCR, but rather due to the discovery of colossal magnetoresistance (CMR) in thin films deposited by PLD [3–5]. $LaMnO_3$ is an antiferromagnetic insulator with manganese in the $+3$ oxidation state. Substitution of La with a divalent cation such as Ca leads to a mixed Mn^{3+}/Mn^{4+} content and the appearance of a temperature-dependent magnetic properties. As the material is cooled, it undergoes an antiferromagnetic/ferromagnetic (AF/F) phase transition. The appearance of the ferromagnetic state is accompanied by quasi-metallic behavior at or near the transition temperature (T_c). This phase transition temperature depends on the $Mn^{3+}:Mn^{4+}$ ratio which is determined by several factors. These include a particular divalent cation, the ratio of RE : M (i.e., x) and an oxygen stoichiometry. The change in resistance with temperature is largest in the quasi-metallic state, just below T_c.

To understand the performance gains realized by using new bolometer materials, it is important to look at competing noise sources that exist in a microbolometer [19]. In general, an integrated infrared focal plane array sensor system has several types of noise. It has been shown [17] that the radiative limited noise equivalent detected temperature (NEDT) for current systems is around 1.5 mK, and devices with a thermal conductance of 1×10^{-7} are well above the background limit at 8–9 mK [17]. Current state-of-the art devices are limited in terms of the detector electronics noise to an NEDT of 50–75 mK. Since this is nearly an order of magnitude higher than the conductive NEDT limit, it is clear that the performance of individual pixel NEDTs could improve nearly linearly with increases in TCR. If we assume that the performance scales linearly, an increase in the TCR of the oxide coating from 2% to 8% results in an increase in the detector sensitivity by a factor of 4. A coating with a TCR of 20% would yield a microbolometer sensitivity that exceeds an MCT detector [19].

We have measured the structure and electrical behavior of single phase, oriented thin films of $La_xCa_{1-x}MnO_\delta$ and $La_xSr_{1-x}MnO_\delta$ deposited by PLD onto $LaAlO_3$. The structure of the deposited films was sensitive to both the substrate deposition temperature and the oxygen pressure. The deposited films have an oxygen-pressure-dependent lattice parameter [19–21]. As-deposited film exhibited a systematic decrease in the unit cell with increasing oxygen deposition pressure. The post-annealing of deposited films also results in a decrease in the lattice parameter as the oxygen stoichiometry increased.

In contrast to the magnetoresistance, the % TCR of deposited films increased with post-deposition annealing. Shown in Fig. 4a is the resistivity and the % TCR for an $La_{0.67}Ca_{0.33}MnO_\delta$ film as-deposited by PLD and which has been post-annealed at 1000°C for 12 h. The peak in the $R(T)$ corresponds to the AF/F phase transition which is at a maximum of 280 K for bulk material. The calculated TCR is ~30% at 210 K. It is desirable that the maximum TCR be near room temperature. This can be done by changing the rare earth and/or divalent cation. The TCR for $La_{0.67}Sr_{0.33}MnO_\delta$ is shown in Fig. 4b. A TCR maximum of only 4% is observed for this material; however, by adjusting the oxygen stoichiometry, the temperature at which this occurs ranges from ~250 to 350 K. The data clearly indicate that by the appropriate choice of the rare-earth, dopant, deposition and post-processing conditions, uncooled IR detectors fabricated from silicon microbridges coated with $RE_xM_{1-x}MnO_\delta$ thin films should have comparable or greater sensitivity than detectors based on HgCdTe.

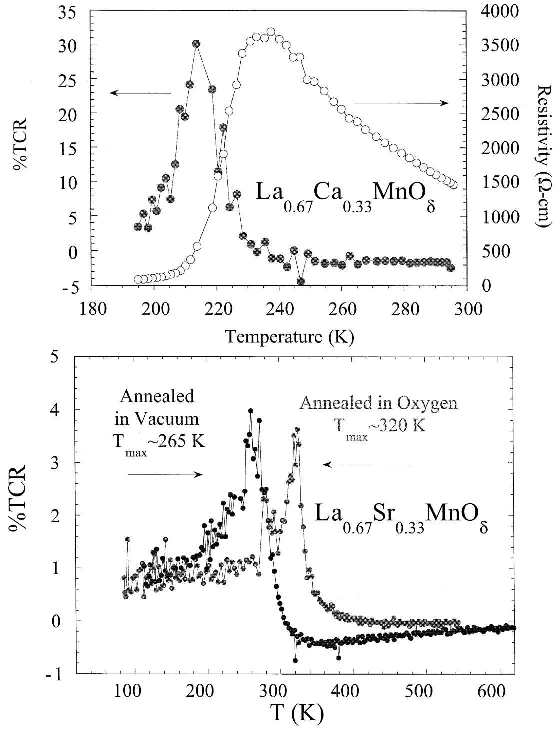

Fig. 4. % TCR for $La_xCa_{1-x}MnO_\delta$ and $La_xSr_{1-x}MnO_\delta$ films that have been annealed. (a) $La_{0.67}Ca_{0.33}MnO_\delta$ annealed at 1000°C. (b) $La_{0.67}Sr_{0.33}MnO_\delta$ annealed in oxygen and vacuum.

5. Conclusions

Pulsed laser deposition (PLD) has been used to deposit a variety of multicomponent electronic ceramics for the development of next-generation electronic devices. Examples include $YBa_2Cu_3O_{7-\delta}$/ferromagnetic multilayers, ferroelectrics and rare earth doped manganite thin films. Spin injection is being used in $YBa_2Cu_3O_{7-\delta}$/ferromagnetic multilayers to produce a local reduction in the superconductivity order parameter. The effect can be used to develop HTS-based digital logic. The electric field effect in $Sr_xBa_{(1-x)}TiO_3$ thin films is being used to develop tunable microwave circuits. Microstructural defects associated with vacancies have been observed in $Sr_xBa_{(1-x)}TiO_3$ films, and these defects have been correlated with dielectric loss in the deposited films. A TCR has been observed in rare earth doped manganite thin films that can be used to increase the sensitivity of uncooled IR focal plane arrays by more than an order of magnitude making them comparable to HgCdTe detectors. These results show the importance of PLD as a tool for research in the physics of thin films, materials science and the fabrication of devices based on electronic ceramics.

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